Characterization of Coal Structure and Low-Temperature Liquefaction Reactions by Pyrolysis-GC-MS in Combination with Solid-State NMR and FTIR.

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INTRODUCTION

Coal conversion into liquids is an extremely complex process and involves both chemical and physical transformations. The dissolution of coal requires homolytic cleavage of bonds to yield free radicals and their immediate stabilization with a hydrogen, otherwise they may recombine or crosslink to form more refractory material. The rate of thermal fragmentation is mainly determined by coal reactivity and reaction conditions. Low-rank coals such as Wyodak subbituminous coal are more reactive than had been thought before. The thermally initiated reactions of coal can take place very rapidly (1,2) and especially for low-rank coals, can occur at lower temperatures (3,4). The previous work in our laboratory has demonstrated that more bonds in low-rank are thermally broken at lower temperature as compared to bituminous coals, and a concept of bond energy distribution has been developed from temperature-programmed pyrolysis (3,4).

It has been also demonstrated that the combination of low-temperature catalytic reaction followed by the high-temperature catalytic reaction using dispersed molybdenum catalyst significantly enhanced coal conversion (5-12). The work presented here is a part of an on-going project on the effects of low-temperature catalytic pretreatment on coal structure and reactivity in liquefaction. Recently, we have demonstrated that the combined use of solid-state NMR and pyrolysis-GC-MS has the potential to reveal the major and minor structural changes in the macromolecular network of coal induced by liquefaction (13, 14). The specific objectives of the present work are to identify the basic changes in coal structure induced by catalytic and thermal pretreatments by using modern analytical techniques.

EXPERIMENTAL

The coal used was a Wyodak subbituminous coal provided by the Penn State Sample Bank (DECS-8). The characteristics of this coal are as follows: 32.4% volatile matter, 29.3 % fixed carbon, 9.9% ash and 28.4% moisture, on a as-received basis; 75.8% C, 5.2% H, 1.0% N, 0.5% S and 17.5% O, on a dmmf basis. The coal was dried in a vacuum oven at 100°C for 2 h before use.

The liquefaction of coal was carried out at 300 and 350°C with and without catalyst (ammonium tetrathiomolybdate,1% wt. of molybdenum of the dmmf coal) and solvents. The solvents used were tetralin, a known H-donor, and 1-methylnaphthalene (1-MN), a non-donor. Liquefaction was carried out in 25 ml microautoclaves using 4 g of coal and 4g of solvent, under 1000 psi H_2 pressure. The reaction time was 30 minutes plus 3 minutes for the heat-up time for autoclave to attain the reaction temperature. After the reaction, the liquid and solid products were separated by sequential extraction with hexane, toluene and THF. After the extraction the THF-insoluble residues were washed first with acetone and then with pentane in order to remove all the THF, followed by drying at 110°C for 6 h under vacuum.

The residues were analyzed by Py-GC-MS, and solid state CPMAS ^{13}C NMR and FTIR techniques as discribed elsewhere (14). The FTIR analysis of the samples was performed on a Digilab FTS 60 FTIR spectrometer. The samples were analyzed as KBr pellets. A accurately weighed amount (approximately 3 mg) of the vacuum dried samples were grinded with pre-weighed amount of KBr (approximately 300 mg). The pellets were pressed under a pressure of 10 tones. The pellets were dried at 100°C under vacuum for 24 h before recording their infrared spectra.

RESULTS AND DISCUSSION

Products Distribution

The liquefaction at 300°C (with H_2, solvent and no catalyst) shows a very small conversion (11-15%). This conversion is not very significant as compared to the total THF-soluble materials (8%) extracted from the raw coal. The presence of solvents (tetralin or 1-methylnaphthalene) seems to have no appreciable effect on the

conversions. The presence of catalyst also did not cause any appreciable increase in the conversion at 300°C, because at low temperature ATTM is less likely to decompose into catalytically active phase.

The results from the liquefaction at 350°C, given in Table 1, show an appreciable effect of catalyst and solvent on the total conversion and quality of the products. In the non-catalytic liquefaction the variation in the total conversion with the solvent is quite significant, with a maximum conversion in presence of tetralin. The total conversions in a solvent-free run and the run with 1-MN are not much different from that at 300°C but with tetralin as a solvent the difference is significant. The presence of catalyst (ATTM) in the liquefaction at 350 °C shows a drastic increase in the total conversion with or without solvent. The larger increase in conversion is in the solvent free liquefaction, though the total conversion is maximum in the presence of tetralin.

Characterization of DECS-8 Wyodak subbituminous coal

The CPMAS ^{13}C NMR spectrum of THF-extracted DECS-8 raw coal, shown in Figure 1, did not show any noticeable difference as compared to that of the unextracted raw coal in terms of aromaticity and functionality. The loss of 8% of organic materials of coal did not produce any apparent changes in its chemical structure. This may not be true for some coals; the THF-extracted sample may display a substantially different spectrum. The NMR spectrum shows two major very broad bands between 0-60 ppm and 90-165 ppm. The first band (0-60 ppm) is due to aliphatic carbons and may also include aliphatic ether carbons. The second region (90-165) is identified as an aromatic region. This band consists of three types of aromatic carbons: an intense peak around 130 ppm (aromatic C), first shoulder at 142 ppm (catechol-like C) and another at 152 ppm (phenolic or aromatic ether C). The other weak and broad bands at 181 and 212 ppm are attributed to carboxylic and ketonic carbons, respectively. The FTIR spectrum of the THF-extracted raw coal was also recorded and compared with that of the unextracted raw coal and there was no significant difference between the two samples.

Figure 2 shows the total ion chromatogram (TIC) from Py-GC-MS of the THF-extracted raw coal up to the retention time 30 minutes, which is a part of the total pyrogram. All the major structural units produced by the flash pyrolysis of the coal other than the alkanes and alkenes are listed in Table 2.The low-rank coals are known to have higher oxygen functionalities: therefore, phenol, alkylphenols, catechol and alkylcatechol are the most intense peaks in the pyrogram of the raw coal. The other minor oxygen-containing compounds identified are indanol, alkyl-indanol and hydroxyindene. Among the most abundant hydrocarbons other than alkanes and alkenes are toluene, xylenes and C_3-benzenes. Indene, alkyl indene, dihydroindene, alkyldihydroindene and alkyl naphthalenes are also identified in minor amounts. There are several intense peaks between 0-2 min (RT) of the pyrogram (Figure 2). These peaks are C_5-C_8 alkanes plus alkenes which coelute. There is another quite intense peak around 25 minutes (RT); it is a branched alkene with m/z 266. There are many more peaks over the whole pyrogram, and selective ion monitoring at m/z 71 indicates that they are long chain alkanes and alkenes. Overall, Py-GC-MS of the THF-extracted raw coal indicates that Wyodak subbituminous coal contains significant amount of oxygen containing structures including phenol, alkylphenols, catechol and other benzenediols as well as indanols. These observations are consistent with our earlier findings (13,14).

Characterization of the residues from the liquefactions.

CPMAS ^{13}C NMR

Figure 1 compares the CPMAS ^{13}C NMR spectra for the THF-extracted raw coal and the coal after liquefaction at 300 and 350°C without any solvent or catalyst. The residue from the reaction at 300°C displays a spectrum very much similar to that of the residue from the raw coal. Integration of the spectrum gives only a slight increase in the aromaticity. The residues produced after the liquefaction at 300°C in presence of solvents with and without catalyst were also analyzed by NMR, and there was no significant difference observed, except a slight increase in the relative intensity of the aromatic region. This increase was relatively less in the case when catalyst was used in the liquefaction reaction.

The residues from runs at 350°C show different spectra as compared to the raw coal. The catecholic (142 ppm) and carboxylic (181 ppm) bands almost disappeared after the run at 350°C and there is a slight decrease in the intensity of the phenolic (152 ppm) band (Figure 1). The residue, obtained from the liquefaction at 350 °C in presence of a solvent (tetralin or 1-MN) were also characterized by NMR. As compared to that of the solvent-free run, the residue from the run with tetralin shows slightly more of catechol-like carbons, but less intense then that of the THF-extracted raw coal. Also a decrease in the aliphatic band is observed. With 1-MN as a solvent the decrease in the aliphatic band is very prominent but the aromatic region shows similar functionality to that of the residue from solvent-free run.

1236

We have seen that the presence of catalyst improves the total conversion at 350°C. However, CPMAS NMR spectra of the samples from catalytic runs appear to be similar to those from thermal runs.

FTIR

The analysis of the residues produced from liquefaction at 300°C showed no marked changes in the FTIR spectrum as compared to that of the THF-extracted raw coal, except a slight decrease in the aliphatic band in the 2950 cm^{-1} region. Using a solvent during the liquefaction also did not cause any appreciable difference in the FTIR spectra of the residues. The residue produced after the liquefaction in presence of catalyst showed a slight decrease in the ether region (1110-1300 cm^{-1}).

Figure 3 shows the FTIR spectra of the residues from liquefaction at 350°C (solvent-free) with and without catalyst, along with that of the residue from the raw coal. There are substantial changes apparent in the structure of coal after liquefaction at 350°C. There is a significant decrease in the carbonyl band at 1700 cm^{-1} and hydroxyl region at 3400 cm^{-1} (presumably carbonyl loss). In presence of catalyst , which improves the total conversion at 350°C, the effect on the ether region is very significant. It appears that catalyst has enhanced the cleavage of the ether bonds in the coal network.

PYROLYSIS-GC-MS

Figure 2 shows the selected retention time region of the Py-GC-MS chromatogram of the THF-extracted raw coal and the residues from the liquefaction at 300 and 350°C (solvent-free). The major peaks which are identified are listed in Table 2. Compared to the pyrogram of the THF-extracted raw coal, all the major species such as phenol, alkylphenols, alkylbenzenes, as well as alkanes and alkenes, are formed from the pyrolysis of the residues from the liquefied coal, but there are apparent differences. A substantial decrease in the intensity of the catechol and alkylcatechol peaks in the pyrogram of the residue from the run at 300°C, and the disappearance of these peaks from the pyrogram of the residue from 350°C run, are the most significant. This change in the residue from the 300°C run is not apparent from NMR, but after liquefaction at 350°C the shoulder at 142 ppm in the CPMAS ^{13}C NMR spectrum disappears completely. From this it is clear that reaction at 300°C did cause some structural changes in the coal network.

The residues from the liquefaction experiments at 300 and 350°C in presence of solvents and with and without catalyst were also characterized by Py-GC-MS. The pyrogram of the residues from liquefaction at 300 and 350 °C in presence of tetralin as solvent (with and without catalyst) are shown in Figure 4. The peaks identified are given in Table 2. The peaks marked with an alphabet in the pyrograms are the new peaks observed after liquefaction in presence of a solvent. An intense methylnaphthalene peak observed here was also seen in the case of a solvent-free run, but with a very low intensity. These new peaks appear to have come from the adduction of solvent because they were not observed in the Py-GC-MS profiles of the residues from the solvent-free runs. When methylnaphthalene was used as solvent, the tetralin and dihydronaphthalene peaks were not observed and the 1-methylnaphthalene peak was very intense, showing that it is due to the solvent . The naphthalene peak was relatively weak in presence of 1-methylnaphthalene, as compared to that in the presence of tetralin . Since the residue was extracted with THF for 24 h and dried, the solvent remaining in the residue must be either chemically bound or physically entraped in the solvent-inaccessible micropores, or both, as also noted in an earlier work (14). In the residue from the liquefaction in the presence of catalyst and solvent, the adduction of solvent was decreased, as shown by the decreased intensity of the solvent peak in the pyrogram. The reason for the decreased adduction of solvent molecules could be due in part to the formation of reduced number of free radicals from the solvent molecules in presence of catalyst. This is also supported by the decreased amount of hydrogen transfer from tetralin and increased amount of hydrogen gas consumption during liquefaction in presence of catalyst compared to that of the catalyst-free experiment.

Table 3 shows the relative ratios of the oxygen-containing units to the alkylbenzenes before and after liquefaction. For oxygen-containing species the areas of the phenol, alkylphenols and catechol peaks were added and for alkylbenzenes, toluene, xylenes and C$_3$-benzenes were used. As compared to that for raw coal, the ratio decreased for the sample from solvent-free run at 300°C, and the sample from the run at 350 °C with 1-MN or without solvent. There ratios show that the presence of solvent does make a difference in the loss of specific type of species from the coal network and it is independent of the catalyst. In solvent-free reaction and with non-donor solvent (1-MN), more oxygen containing species are lost during liquefaction. In presence of tetralin during the liquefaction, this ratio did not decrease much from that of the raw coal and is highest as compared to the others.

The results of this work, though preliminary, have shown that there are significant changes in the coal structure as a consequence of the low-temperature catalytic pretreatments. Further work on the identification of specific changes in the coal structure is now in progress.

ACKNOWLEDGEMENT

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TABLE 1. Products distribution (dmmf wt %) for the liquefaction at 350°C with and without catalyst.

Solvent	Gas	Oils	Asphaltenes	Preasphaltenes	Total Conversion
Thermal					
none	3.3	2.1	2.6	4.5	12.5
Tetralin	4.2	4.1	7.6	10.0	25.9
1-MN	4.0	1.1	5.8	7.4	18.3
Catalytic					
none	3.0	10.0	5.4	11.4	29.8
Tetralin	3.0	10.2	12.9	10.6	36.4
1-MN	2.6	6.1	10.1	12.3	31.1

TABLE 2. Major identified peaks in pyrograms.

No.	MW	Identified Compounds
1	92	Toluene
2	106	p-Xylene
3	106	o-Xylene
4	120	C_3-benzene
5	120	C_3-benzene
6	120	C_3-benzene
7	94	Phenol
8	118	Indane
9	116	Indene
10	108	o-Cresol
11	108	m-+p-Cresol
12	132	Methylindane
13	130	Methylindene
A*	132	Tetralin
14	122	Ethylphenol
B*	130	Dihydronaphthalene
15	122	Ethylphenol
16	122	Dimethylphenol
C*	128	Naphthalene
17	146	Dimethylindene
18	122	Dimethylphenol
19	136	C_3-Phenol
20	110	Catechol
21	136	C_3-Phenol
22	144	Dimethylindene
23	136	C_3-Phenol
24	124	Methylcatechol
25	124	Methylcatechol
D*	142	2-Methylnaphthalene
E*	142	1-Methylnaphthalene
26	110	1,3-Benzenediol
27	134	Indanol
28	134	Indanol
39	132	Hydroxyindene
30	138	C_2-Catechol
31	156	C_2-Naphthalene
32	170	C_3-Naphthalene

* The compounds identified in Py-GC-MS profiles (Figure 4) of the residues from the liquefactions in presence of tetralin.
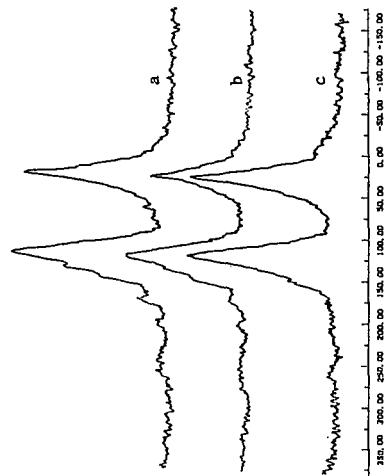

FIGURE 1 CPMAS ^{13}C NMR spectra of (a) THF-extracted raw coal and the residues from the solvent free thermal liquefactions at (b) 300°C, and (c) 350°C.
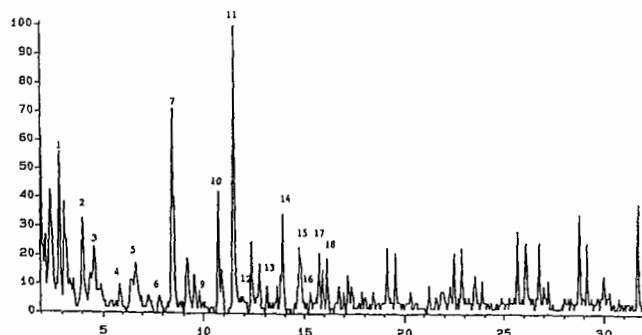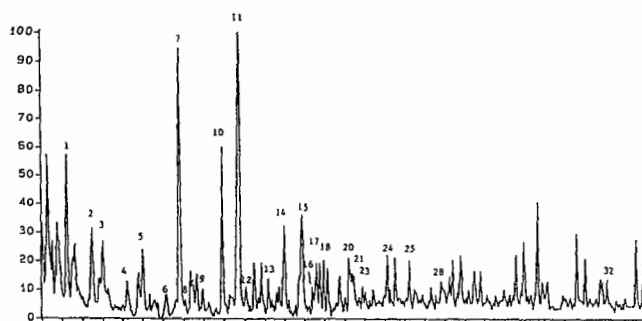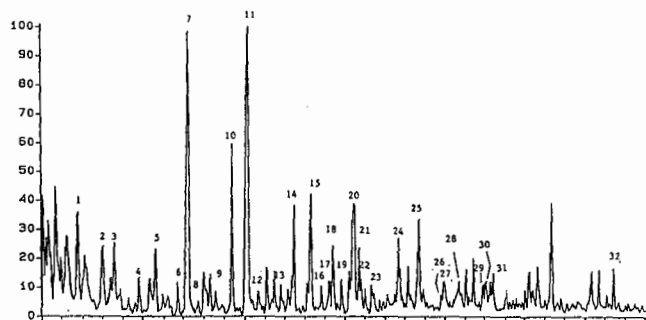
FIGURE 2.   Py-GC-MS profiles of (a) THF-extracted raw coal and the residues from the thermal liquefactions at (b) 300°C, and (c) 350 °C.

TABLE 3. Ratios of the amount of the oxygen-containing units to the
alkylbenzene units.

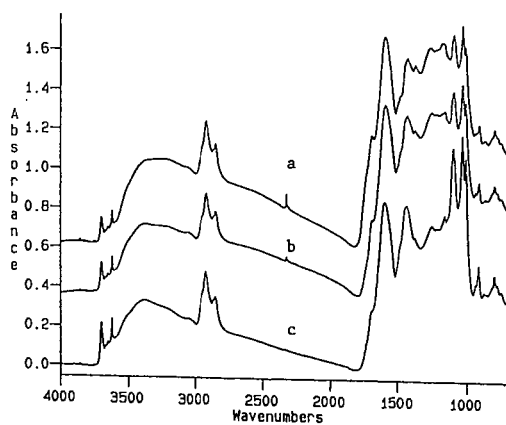| Temperature (°C)	Solvent	Ratio Phenolic/Alkylbenzenes	
		Thermal	Catalytic
Raw Coal		3.6	
300	none	2.4	2.5
300	Tetralin	3.5	3.1
300	1-MN	3.6	3.2
350	none	2.3	2.4
350	Tetralin	3.2	3.1
350	1-MN	1.9	2.3

FIGURE 3.   FTIR spectra of (a) THF-extracted raw coal and the residues from the solvent-free,
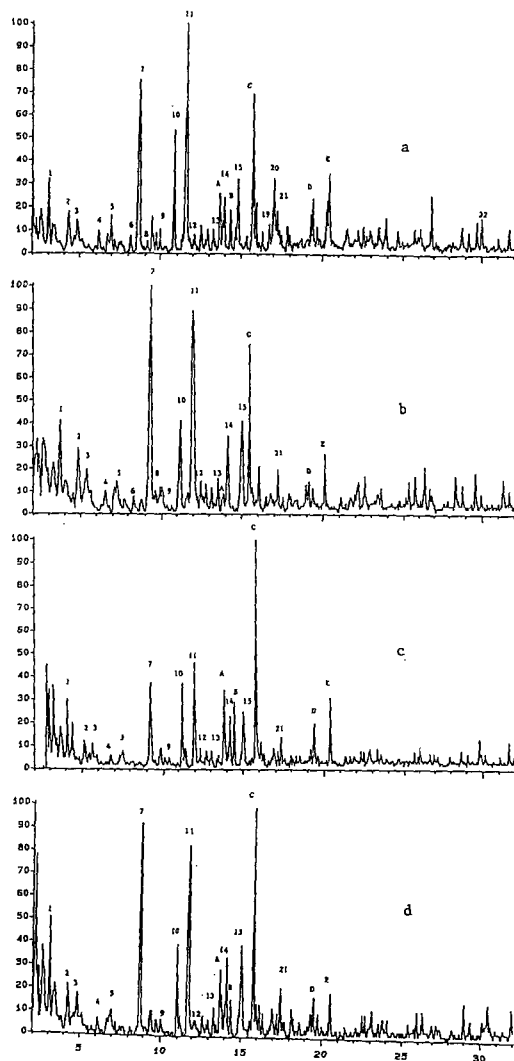(b) thermal, and (c) catalytic liquefactions at 350°C

FIGURE 4.   Py-GC-MS profiles of the residues from the liquefactions in presence of tetralin, (a) thermal, (b) catalytic at 300°C, and (c) thermal, (d) catalytic at 350°C.

1242